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# Infrared Physics & Technology

journal homepage: www.elsevier.com/locate/infrared



# On the heating modulation frequency dependence of the photopyroelectric signal in experiments for liquid thermal characterization

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#### ARTICLE INFO

Article history: Received 30 May 2011 Available online 30 August 2011

Keywords:
Photopyroelectric technique
Photoacoustic
Thermal waves
Heat transfer
Thermal effusivity

#### ABSTRACT

A pyroelectric sensor can be seen as a layered system consisted on a pyroelectric material sandwiched between two thin metal layers acting as electrical contacts for measurements of the voltage drop that can be induced by heating. This kind of sensor can be used as a detector of electromagnetic radiation but also for thermal characterization of materials using the photopyroelectric technique. In this work we perform a theoretical analysis based in the so-called thermal wave approach to show that, when this sensor is heated periodically by the absorption of intensity modulated light by one of the metalized surfaces, while the other metal surface is in contact with a liquid sample, the resulting pyroelectric voltage signal amplitude enhances respecting the one resulting from the bare sensor, for certain values of the modulation frequency. This contradicts the intuitively expectation based in the assumption that the sample provides a new channel for heat conduction, thereby decreasing the pyroelectric temperature. We will show that the back and forth propagation and the superposition of thermal waves through the metal coatings must be taken into account in order to explain the observed behavior. The proposed model was experimentally tested for water and glycerin samples, and using a polyvinylidene difluoride (PVDF) polymer film, with Ni–Cu metal electrodes, as a pyroelectric sensor.

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## 1. Introduction

In the last years the photopyroelectric (PPE) technique [1] in its several experimental configurations has become great attention due its possibilities to perform the thermal characterization of materials [1]. The pyroelectric (PE) sensor is usually a polyvinyledene difluoride (PVDF) polymer film with metalized surfaces serving as electrodes providing an output voltage, but a pyroelectric ceramic crystal (e.g., LiTaO<sub>3</sub>) can be used as well [2]. In one of the more used configurations, the analyzed sample is placed in intimate thermal contact with one of the metal coated surfaces of the sensor, while a periodical intensity modulated light beam impinges on its opposite metalized side, which acts as a light absorber. Following the absorption of light energy, the PE sensor temperature fluctuates periodically at the modulation frequency of the incident beam (these temperature oscillations are the so-called thermal waves) thereby generating a voltage, whose amplitude at a given frequency can be measured using a Lock-in amplifier. This experimental variant is often called the front or inverse PPE technique [3]. Due to the good thermal contact that can be achieved between liquids and detector, the majority of the published works concern the characterization of these kind of materials. The technique has been found mainly suitable for thermal effusivity (e) measurements and phase transitions monitoring [4]. Applications in the fields of food characterization [5], study of liquid mixtures [6], thermal characterization of colloidal suspensions of nanometric sized particles (the so-called nanofluids) [7], among others, demonstrate the usefulness of this photothermal (PT) technique. Because the measured voltage signal is proportional to the temperature fluctuation in the PE material, with an instrumental transfer function that is a function of the modulation frequency, a normalization procedure is in many cases necessary. This is often performed by dividing the signal amplitude measured in the presence of a sample by that measured with the bare detector. The resulting quotient will be denoted hence forth as the normalized signal. In the majority of works performed at very low modulation frequencies it is found that the normalized signal becomes lower than the unit, an expected behavior since in the presence of a liquid sample the heat developed by the absorption of radiation at the metal coating will flow through the PE material to the sample, which will acts as a heat sink. As a result, the PE temperature will be less than that for the situation in which no liquid is present. However, some authors have reported [8-10] a behavior that contradicts the one described above at higher frequencies. They show an increase of the normalized signal above the unity in certain

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